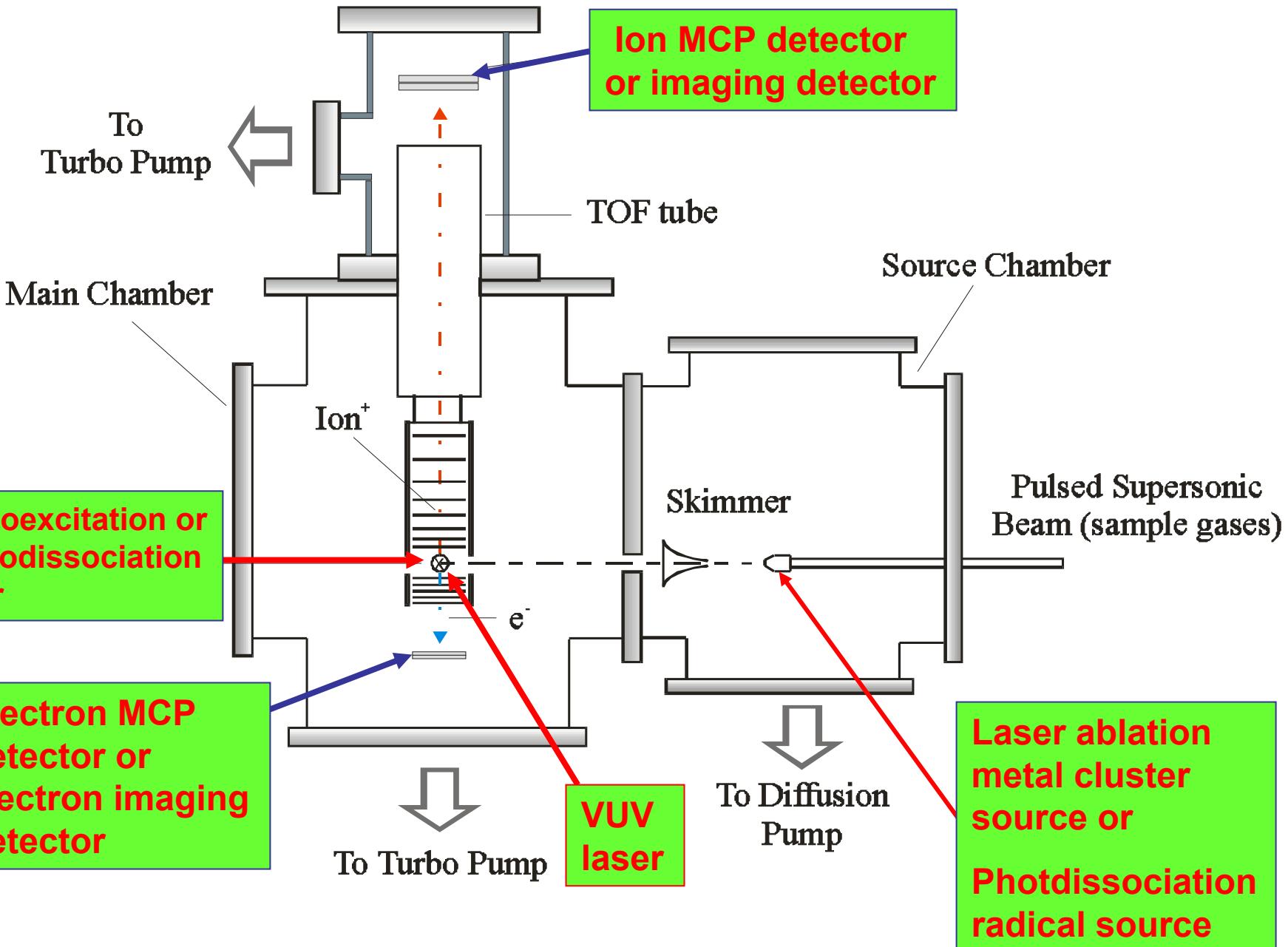


Atomic and Chemical Physics Working Group

Summary Viewgraphs

Summary of AMO/ChemPhys Experimental Requirements

PI/ Affiliation	Experiment	λ- range (nm)	Pulse energy (μJ)	Pulse length (fs)	Spot size (μm)	Energy FWHM (%)	2 nd laser
Mark Knickelbein /ANL	Photo-absorption of clusters	55-200	100	500	5000	2.5	ArF
Laurie Butler/U. Chicago	Photo-dissociation of radicals	65-180	200	500 or longer	<500	1.0	ArF
Steve Pratt/ ANL	Double photo-ionization	10-100	200	<300	<500	0.3-1.0	
Cheuk Ng/ UCDavis	Spectroscopy of radicals and ions	55-200	200	200-500	2000	0.3-2.5	IROPO



Photoabsorption of Metal Clusters and Complexes

Mark B. Knickelbein (Argonne Nat. Lab.)

- **Ionization energies (IEs):**
Photoion spectra of metal clusters, complexes, and transient species with $\text{IEs} > 6.4 \text{ eV}$
- **Photoabsorption cross sections (IR and visible):**
Ion-(or photoelectron-)depletion measurements of clusters and nanoparticles via VUV ionization
- **Laser pump-VUV-probe studies:**
Cluster photodissociation
- **VUV-electron detachment studies:**
Valence bands of (neutral) cluster species

Ultrafast Pump-Probe Spectroscopy (Unique experiments:wave packet dynamics)

Pump: Photodissociation



Probe: Delayed-photoelectron detection



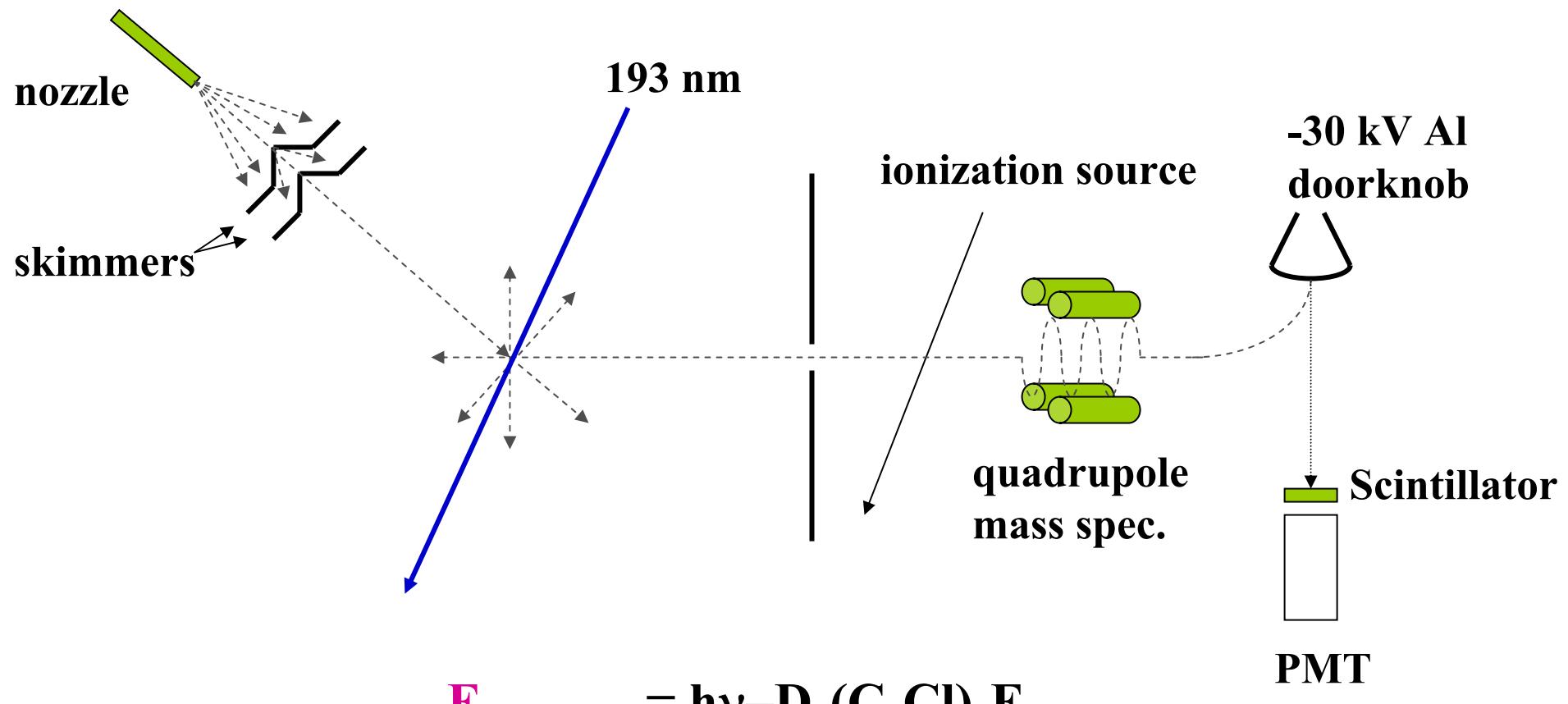
Low repetition rate: not suitable for electron-ion coincidence detection

Laser Photodissociation Dynamics

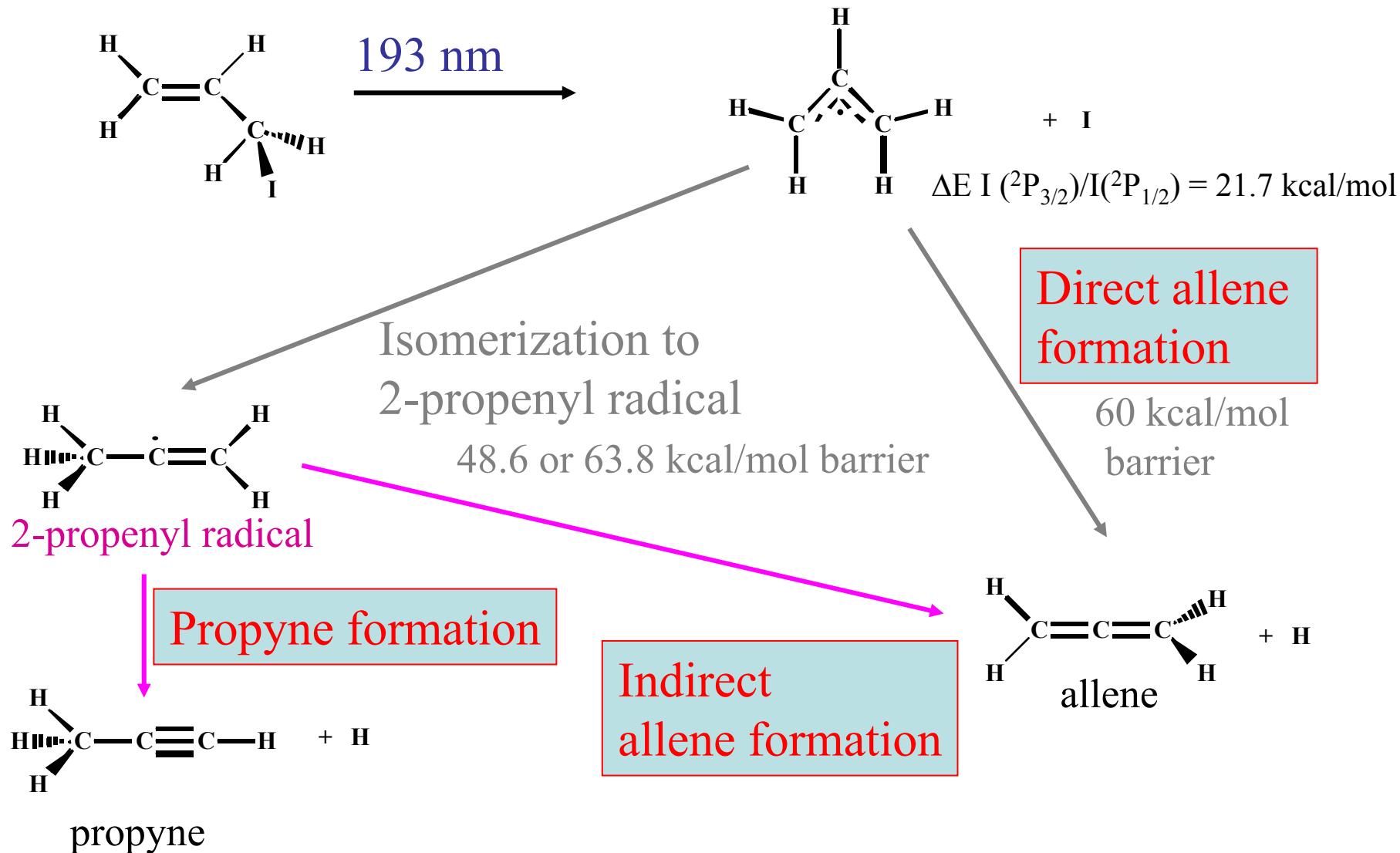
Laurie B. Butler (Univ. of Chicago)

- **Photofragment angular distribution:**
Information about excited surfaces
- **Photofragment time-of-flight distribution:**
Product channel identification by
momentum matching
Product translation (internal) energy distribution
Potential barriers for dissociation
- **VUV photoionization sampling:**
To resolve competing dissociation channels of
free radical isomers

Laser photofragmentation TOF mass spectrometry



Allyl Radical Reaction Paths

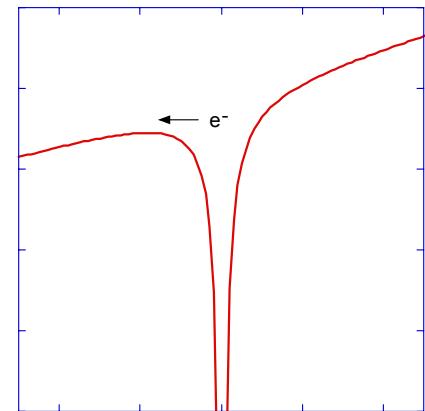


Non-sequential double ionization and inner-valence holes (low field)

S. T. Pratt (*Argonne Nat. Lab.*)

The ionization mechanism depends on the adiabaticity, or **Keldysh** parameter, where I_p is the ionization potential and U_p is the ponderomotive potential. The parameter is essentially the ratio of the tunneling time to the optical period.

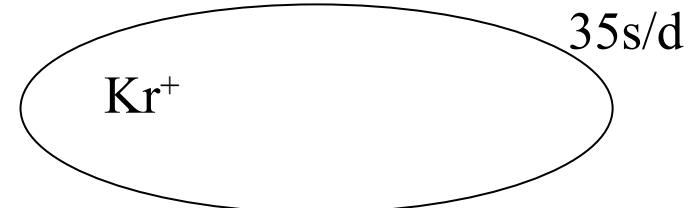
$$\gamma = \left(\frac{I_p}{2U_p} \right)^{1/2}$$



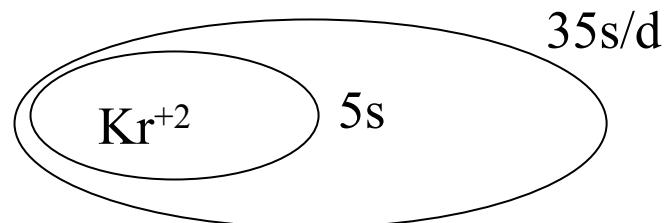
For the parameters of ALFF (100 nm, 200 μ J, 300 fs, 10 μ m diameter focal spot), γ is ~ 2.5 , and thus clearly in the multiphoton regime.

Resonant Three-Photon Ionization of Kr at 112830.0 cm⁻¹ (88.6 nm)

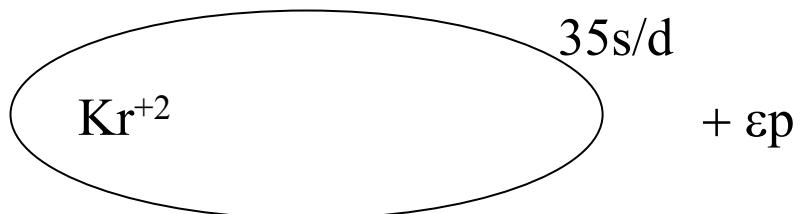
Photon 1: $4s^24p^6 \rightarrow 4s^24p^5(Kr^+ \ ^2P_{3/2})35s/d$



Photon 2: $4s^24p^5(Kr^+ \ ^2P_{3/2})35s/d \rightarrow$
 $4s^24p^4(Kr^{+2} \ ^3P)5s,35s/d$



Photon 3: $4s^24p^4(Kr^{+2} \ ^3P)5s,35s/d \rightarrow$
 $4s^24p^4(Kr^{+2} \ ^3P)35s/d + \epsilon p$



and, as a satellite

$4s^24p^5(Kr^+ \ ^2P_{3/2})5s,35s/d \rightarrow$
 $4s^24p^4(Kr^{+2} \ ^3P) + \epsilon p + \epsilon' s/d$

$Kr^{+2} + \epsilon p + \epsilon' s/d$

Photoelectron Spectroscopy

- Direct ionization leaving Kr^+ in an $n \sim 35$ Rydberg state
- Shake up and final state interactions to give $\text{Kr}^{+2} + \text{es} + \text{ep}$
- Photoelectron imaging would give angular distributions

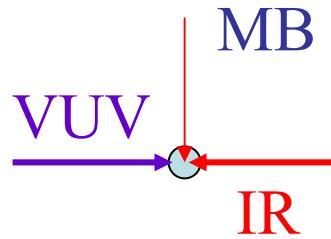
Total three-photon energy is ~ 3.4 eV above the double ionization threshold

Spectroscopy of Radicals and Ions

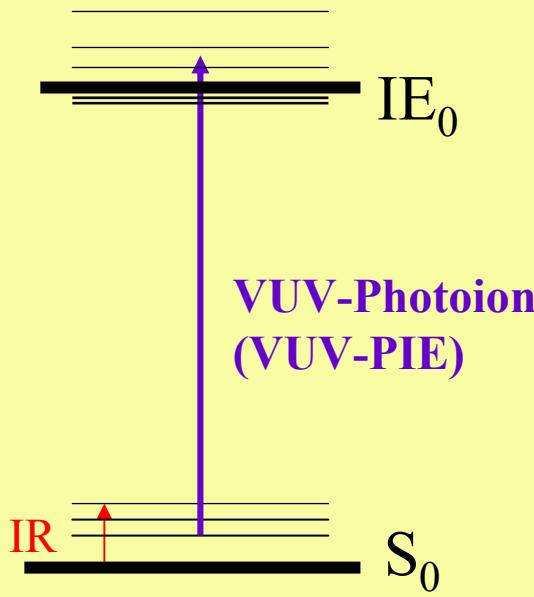
Cheuk-Yiu Ng (UC Davis)

- Infrared Spectroscopy of Radicals
IR-VUV photoion (scan IR, VUV fixed):
 IR spectra neutrals (mass identification)
IR-VUV-photoelectron (scan IR, fixed VUV):
 IR absorption (species specific)
- Infrared Spectroscopy of Ions
VUV-IR photoion (fixed VUV below IE, scan IR):
 IR spectra of ions
Photo-induced Rydberg Ionization (PIRI)

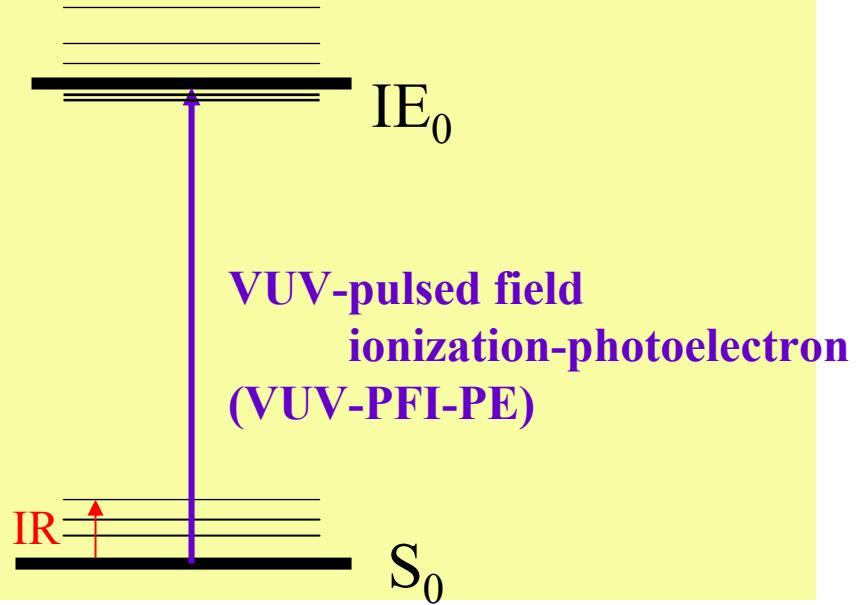
Spectroscopy Experiments



IR spectroscopy of neutral molecules

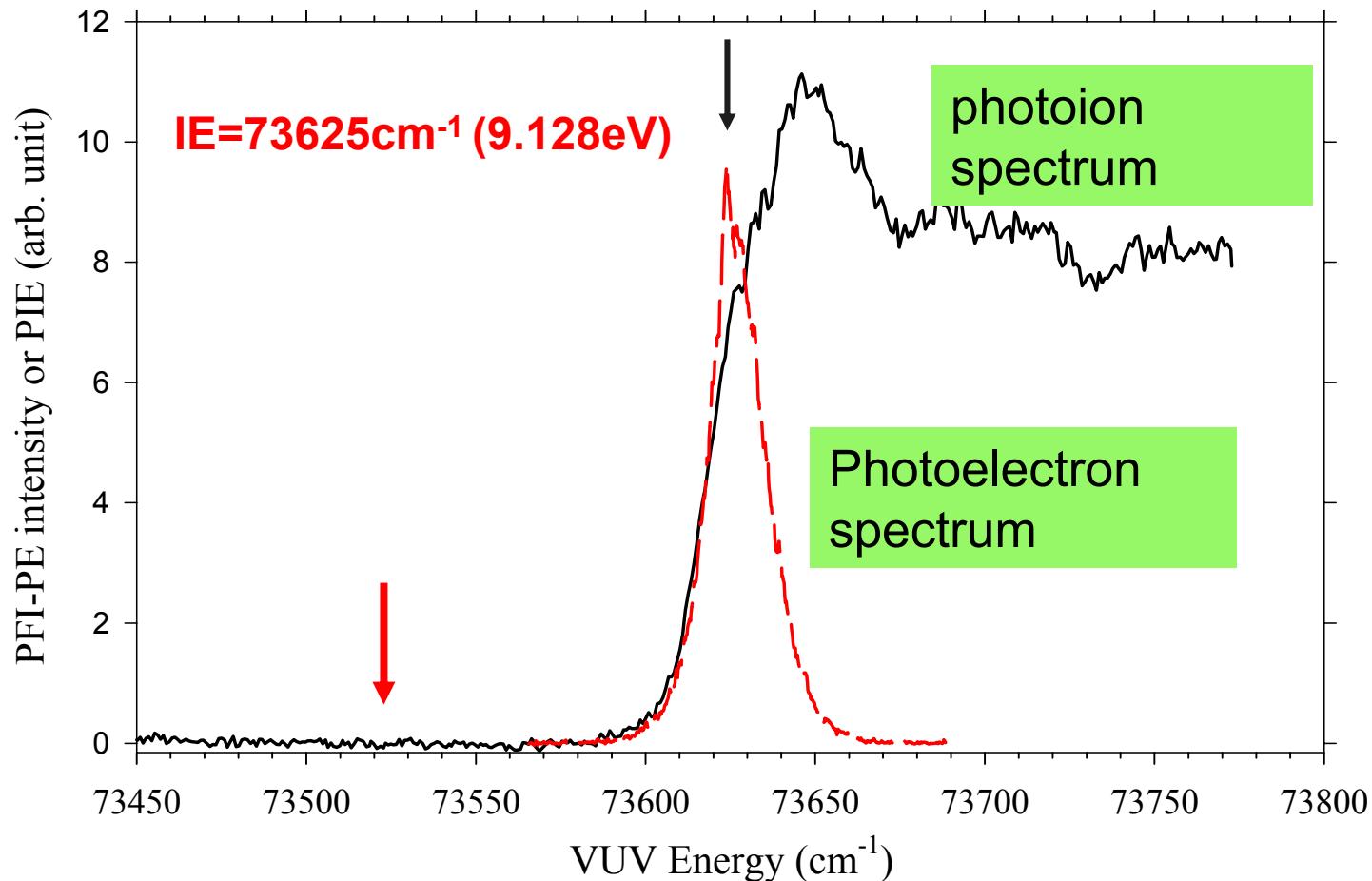


Fix VUV and scan IR
IR spectrum as PIE spectrum



Fix VUV-PFI-PE and scan IR
IR spectrum as depletion spectrum

Photoion and photoelectron spectra for trans-2-butene



Photoelectron depletion spectrum for trans-2-butene

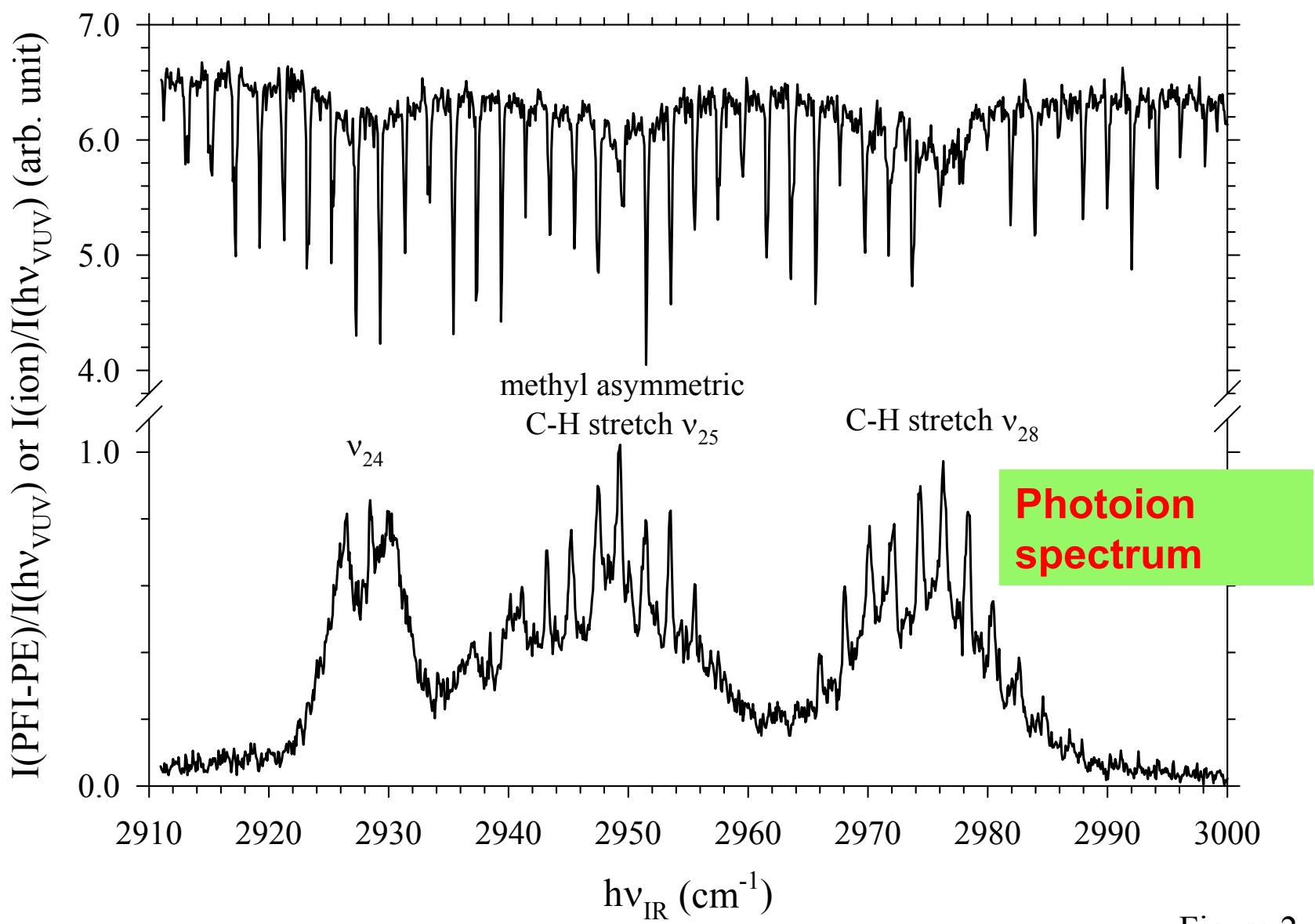
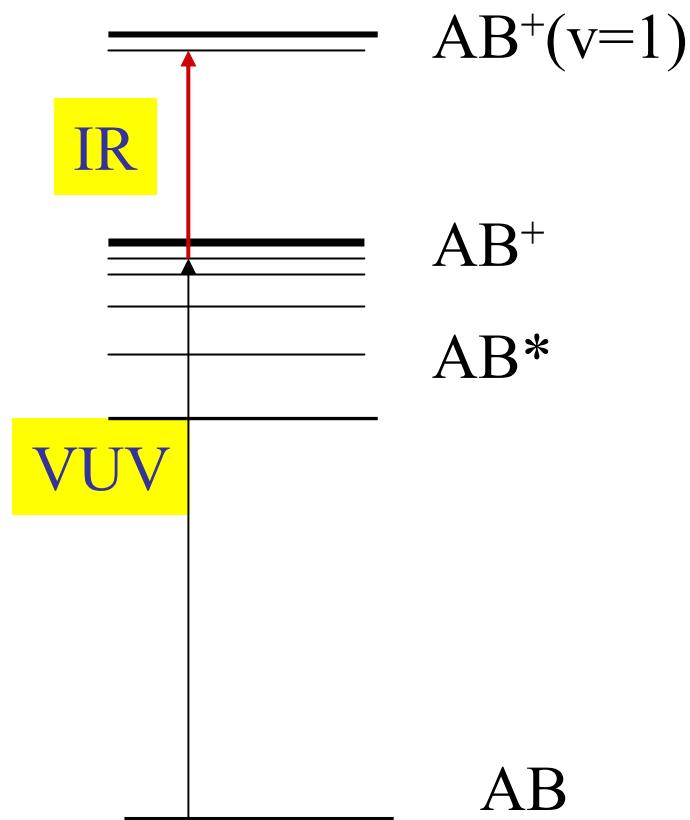


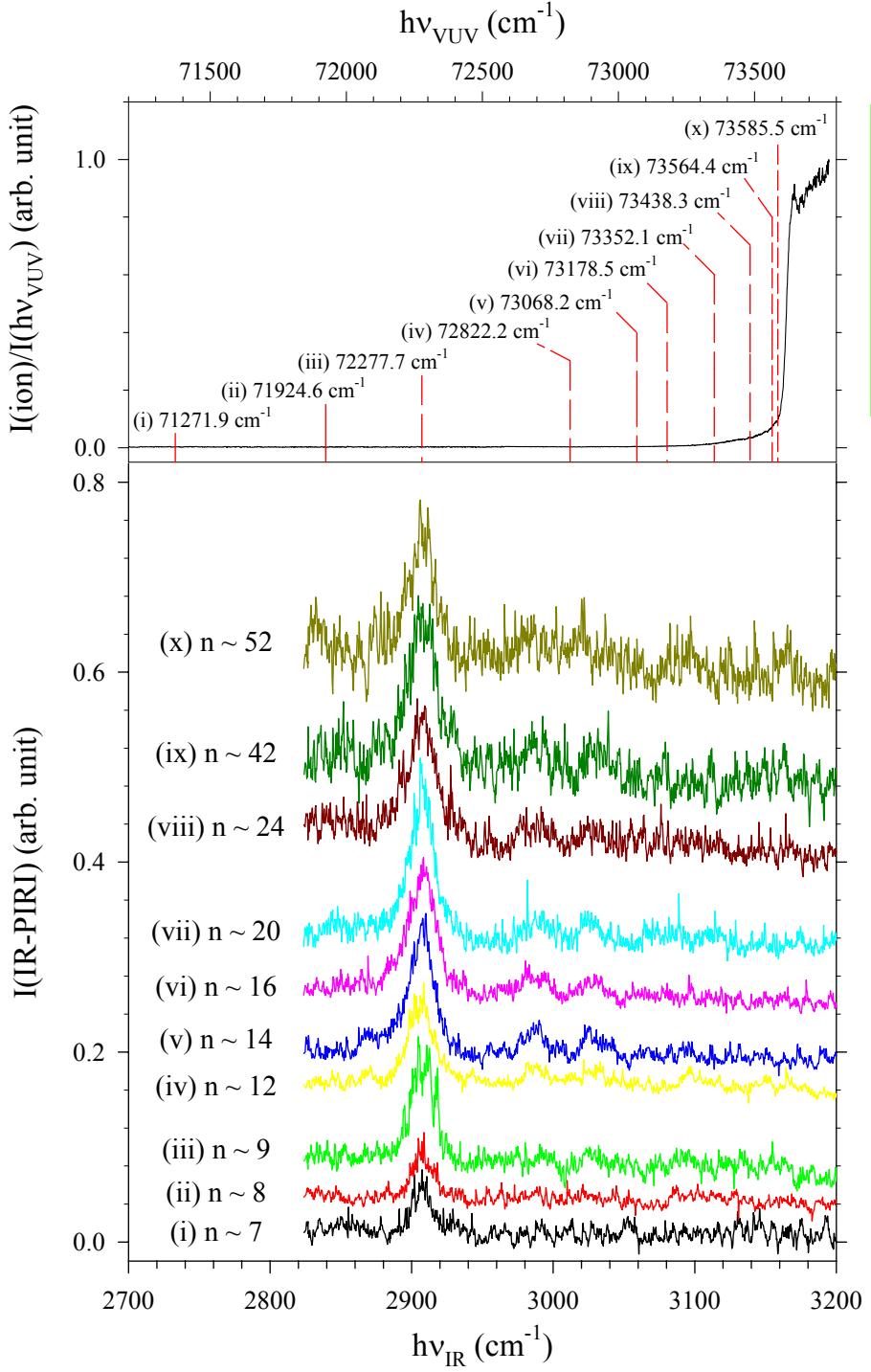
Figure 2



VUV-IR photo-induced Rydberg Ionization



Applications:
Spectroscopy of ions



VUV-IR Photo-induced Rydberg Ionization (PIRI) spectra of *trans*-2-butene (*trans*-CH₃C=CCH₃)

VUV prepared *trans*-2-butene to high Rydberg states $n \approx 7$ -52.

IR laser is scanned to excite ion core to C-H stretching mode, which induced autoionization.

Peaks are observed at the same IR frequency, indicating that n is conserved.